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(54) COATED METAL ARTICLE AND METHOD OF
MAKING THE SAME

- (71) We, HAVEG INDUSTRIES, INC., a Corporation of the State of Delaware, United States of America, located at 900 Greenbank Road, Wilmington, Delaware 19808, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a metal article having a mixed crystalline-glass glass coating and to a method of producing the same.
- 15 Glass or vitreous enamel coatings are frequently applied to metal articles, such as steel, to prevent corrosion of the metal base. In the normal glass coating procedure the glass frit, along with a mill addition, is applied to the surface of the steel in the form of a slip or slurry. After drying of the slip, the coated
- 20 article is heated or fired at an elevated temperature, generally in the range of 1500 to 1800°F, to fuse the glass.
- 25 Silica is the major constituent in most common glasses and when the glass coated article is exposed in service to highly corrosive media, a high silica content, in the range of 70 to 85% by weight, is desired because the silica increases the resistance of the glass to chemical attack.
- 30 It is also recognized that a devitrified glass has good impact and shock resistance as well as toughness, but, in general, devitrified glass lacks corrosion resistance due to the fact that the devitrified particles are composed
- 35 primarily of silica and the amorphous glass matrix, being depleted of silica, has a low resistance to corrosive attack.
- 40 In the past it has been proposed to combine a high-silica corrosion resistance glass frit with a devitrifiable glass frit in an attempt to produce a glass coating having good impact resistance along with good corrosion resistance. In

a process of this type, the common procedure has been to mill the corrosion resistant glass frit and the devitrifiable glass frit together and apply the mixed frit to the metal article. After firing of the coated article to fuse the glass, the glass coated article is then subjected to a further heat treatment at a temperature beneath the firing temperature to develop the devitrified particles. As a result of this final heat treatment, a three phase system is produced consisting of (i) the amorphous glass matrix of the devitrifiable glass which matrix is depleted of silica by removal of the devitrified particles, (ii) the devitrified particles, and (iii) the corrosion resistant glass. As the amorphous glass matrix, which is depleted of silica, has poor corrosion resistance, this provides a weak link in the corrosion resistance of the coating.

45 It has also been proposed in the past to separately coat a metal article with both a devitrifiable glass and a corrosion resistant glass. In United States Patent No. 3,361,588, a process of this type is disclosed in which the steel is initially coated with a devitrifiable glass which is subsequently devitrified by heat treatment. Following this, a corrosion resistant glass frit is applied to the devitrified glass and subsequently fired. However, a process of

50 that type requires two separate heat treatments of the metal article or vessel which increases the overall cost of the process.

55 According to the present invention there is provided a coated metal article comprising a base of ferrous metal or other metal having a coefficient of thermal expansion similar to that of steel, and a frit composition disposed on a surface of the base and comprising a mixture of (a) up to 60% by weight of a devitrified glass frit composed of an amorphous glass matrix and containing devitrified crystalline particles, and (b) at least 40% by weight of a

corrosion resistant glass frit containing 63—80%, by weight of silica, said frit composition being such that when subsequently fired to fuse the composition to the metal, said amorphous glass matrix will at least partially dissolve in said corrosion resistant glass frit during said firing.

The invention also provides a method of coating an article of ferrous metal or other metal having a coefficient of thermal expansion similar to that of steel, which comprises devitrifying a devitrifiable glass frit to produce a devitrified frit composed of an amorphous glass matrix and devitrified crystalline particles dispersed within said matrix, mixing up to 60%, by weight of said devitrified glass frit with at least 40%, by weight of a corrosion resistant glass frit containing 63—80% by weight of silica to provide a frit mixture, applying said frit mixture to the metal article, and firing said article at a temperature sufficiently high to fuse said frit to said metal article, so that said amorphous glass matrix at least partially dissolves in said corrosion resistant glass frit during said firing.

The present invention is directed to the production of a coated metal article on which the resulting crystalline-glass coating not only has improved impact resistance and toughness but also has excellent resistance to corrosive attack. A devitrifiable glass frit is initially dry milled and subsequently heat treated at an ele-

vated temperature and for a sufficient period of time to substantially fully devitrify the devitrifiable portion of the frit. The devitrification results in the development of minute silicate crystals in a matrix of amorphous glass. Following the devitrification, the devitrified frit is wet milled with a conventional corrosion resistant glass frit containing 63—80%, by weight of silica. The milled slurry is applied to the metal article and after drying, the article is fired at an elevated temperature for a period of time sufficient to fuse the glass.

The devitrifiable frit is a conventional glass frit capable to devitrifying during heat treatment. The devitrifiable frit may have the following composition in weight percent:

Li_2O	1—25%	50
Al_2O_3	0—30%	
SiO_2	60—80%	
Na_2O	0—5%	
MgO	0—5%	
CeO_2	0—10%	
TiO_2	0—5%	
ZrO_2	0—5%	
PbO	0—5%	
CaO	0—10%	

Specific examples of frits capable of devitrifying and falling within the above range of composition are as follows in weight percent:

	1	2	3
Li_2O	15.0	1.5	8.0
Al_2O_3	25.0	—	2.0
SiO_2	60.0	75.0	75.0
Na_2O	—	5.0	—
MgO	—	3.0	3.0
CeO_2	—	8.5	—
TiO_2	—	—	3.0
ZrO_2	—	3.0	—
PbO	—	4.0	—
CaO	—	—	9.0

The devitrifiable frit is initially dry milled by conventional milling equipment. The particle size of the milled frit is not critical, but is generally less than 35 mesh U.S. standard sieves.

- 5 Following the milling, the frit is heated to an elevated temperature for a period of time sufficient to substantially fully devitrify the devitrifiable portion of the frit. The specific 10 temperatures and times involved in the devitrification depend on the composition of the frit, but generally the temperatures will be in the range of 1000° to 1600°F and the time employed at this temperature is usually in the 15 range of 1 to 2 hours. During this heat treatment, silicate particles crystallize out of the amorphous glass matrix. It is desired to crystallize or devitrify the whole of the devitrifiable portion of the frit, and in most cases, the crystals, after devitrification, comprise at 20 least 50%, and in most cases from 60 to 85%, by weight of the devitrified frit.

The devitrified crystals have a size less than 10 microns and in most instances have a

particle size in the range of 0.1 to 2.0 microns.

Following the devitrification, the devitrified frit is wet milled with a corrosion resistant glass frit containing 63—80% by weight of silica. The corrosion resistant glass frit may have the following formulation in weight percent:

<chem>SiO2</chem>	63—80%	25
<chem>TiO2</chem>	0—2%	
<chem>ZrO2</chem>	0—8%	
<chem>CaO</chem>	0—2%	35
<chem>Li2O</chem>	1—5%	
<chem>Na2O</chem>	8—17%	
<chem>K2O</chem>	0—7%	
<chem>MgO</chem>	0—2%	
<chem>F2</chem>	0—3%	40
<chem>CoO</chem>	0—1.25%	
<chem>MnO</chem>	0—1.50%	
<chem>NiO</chem>	0—1.50%	

Specific examples of corrosion resistant frits falling within the above range of composition 45 are as follows in weight percent:

	1	2	3
<chem>SiO2</chem>	72.5	73.5	75.0
<chem>TiO2</chem>	1.0	—	—
<chem>ZrO2</chem>	4.0	5.5	4.5
<chem>CaO</chem>	1.0	2.0	1.5
<chem>Li2O</chem>	2.5	3.0	3.0
<chem>Na2O</chem>	13.5	14.0	12.5
<chem>K2O</chem>	2.0	—	1.0
<chem>MgO</chem>	1.0	—	1.0
<chem>F2</chem>	—	2.0	—
<chem>CoO</chem>	0.5	—	0.5
<chem>MnO</chem>	1.0	—	0.5
<chem>NiO</chem>	1.0	—	0.5

- 50 In most cases the corrosion resistant glass frit is a non-devitrifiable frit, but this is not essential, and the corrosion resistant frit may devitrify to some extent. Even if the corrosion resistant frit is capable of devitrifying, it will not devitrify during the firing period because the metal article is not held at the firing 55 temperature for a sufficient period of time to enable a devitrifiable corrosion resistant frit to devitrify.

Mill additions are normally added to the glass frit and are of conventional types: they may be sodium nitrite, sodium aluminate or a clay, such as bentonite.

The devitrifiable frit constitutes up to 60% by weight of the dry frit mixture and is preferably from 20 to 50% of the dry mixture.

The devitrifiable frit and the corrosion 65 resistant glass frit are preferably wet milled as a water suspension. However, in some cases

the two frits can be dry milled and subsequently applied to the metal article as a dry dust coating. The particle size of the milled frit mixture is not critical and follows conventional enamelling techniques. Generally, up to 85% by weight of the milled frit particles will pass through a 200 mesh U.S. standard sieve.

The wet milled frit mixture can be applied to the metal base by any conventional technique, for example, by spraying, dipping, slushing, or brushing. After application to the metal base, the coating is dried to evaporate the water.

10 The metal base can be steel or any other metal having a coefficient of thermal expansion similar to steel. More specifically, the metal base can be carbon steel such as SAE 1010—1030, stainless steel, or the materials sold under the registered trade marks, Inconel and Hastalloy C—276.

15 The glass coated metal base is preferably fired at a temperature in the range of 1400° to 1700°F, and usually in the range of 1500° to 1600°F, for a period of 5 to 15 minutes to fuse the glass to the metal. During the firing, the amorphous glass matrix of the devitrifiable frit at least partially dissolves in the corrosion resistant glass so that the silica-depleted amorphous glass matrix is substantially eliminated in the resulting glass coating. After firing, the coating is composed of devitrified crystals and a blend of the corrosion resistant glass and the glass matrix of the devitrifiable frit. As the 20 glass matrix of the devitrifiable frit is not present as a separate phase in the final product, the corrosion resistance of the glass coating is substantially improved, and yet the presence of the devitrified particles improves the thermal shock resistance as well as the toughness of the glass coating.

25 Devitrifying the devitrifiable glass frit prior to applying the frit to the metal article enables a wider range of heat treatment to be employed in the devitrification operation. If the frit was to be devitrified on the metal article after firing, the range of heat treatment would be limited, for it is not feasible to heat treat some metal parts for long periods without warping.

30 A further disadvantage of prior art processes in which devitrification was carried on after application of the glass to the metal article or vessel is that some portions of the vessel will heat differently from other portions with the result that varying degrees of devitrification of the glass will be obtained, thereby resulting in varying physical properties in the glass coating. This problem is eliminated by 35 the present invention, since the frit is devitrified in bulk before being applied to the vessel, so that the vessel is not subjected to the prolonged devitrification heat treatment.

40 By subjecting the frit in bulk to the devitri-

fication heat treatment, it is also possible to use more refractory frit compositions containing higher proportions of silica and having higher devitrification temperatures. High silica content refractory compositions cannot be used if the devitrification is carried on after the frit is applied to the vessel, for prolonged heating at the high devitrifying temperature may adversely effect the physical properties of the vessel.

45 Specific examples of the process of the invention will now be given.

EXAMPLE No. 1

A devitrifiable frit was prepared having the following composition in weight percent:

Li ₂ O	8.0	80
Al ₂ O ₃	2.0	
SiO ₂	75.0	
MgO	3.0	
TiO ₂	3.0	
CaO	9.0	85

The frit was milled and heated in bulk to a temperature of 1350°F and held at this temperature for a period of one and one-half hours to devitrify the frit. Following devitrification, the frit was air cooled to temperature.

40 parts of the devitrified frit were milled with 60 parts of a corrosion resistant glass frit together with a mill addition, which consisted of 3 parts clay, 0.2 part of colloidal aluminium oxide, 0.1 part of sodium aluminate, and 43 parts of water.

45 The corrosion resistant glass frit had the following composition in weight percent:

SiO ₂	72.5	100
TiO ₂	1.0	
ZrO ₂	4.0	
CaO	1.0	
Li ₂ O	2.5	
Na ₂ O	13.5	
K ₂ O	2.0	105
MgO	1.0	
CoO	0.5	
MnO	1.0	
NiO	1.0	

50 In the wet milling procedure, the devitrified frit and mill additions were initially melted for one hour and then the corrosion resistant frit was added and the milling was continued for an additional one and one-half hours. After milling the frit mixture had a particle size such that less than 3% was retained on a 200 mesh U.S. standard sieve.

55 The milled slip was then sprayed onto the ground coated surface of a low carbon steel plate and dried under infrared lamps.

60 After drying the coated plate was fired at a temperature of 1540°F for 9 minutes.

65 The resulting coated steel plate had good

impact and shock resistance as well as excellent corrosion resistance.

EXAMPLE No. 2

A devitrifiable frit was prepared having the following composition in weight percent:

	Li ₂ O	8.0
	Al ₂ O ₃	2.0
	SiO ₂	75.2
	MgO	3.0
10	TiO ₂	3.0
	CaO	9.0

The frit was milled and heated in bulk to a temperature of 1550°F and held at this temperature for a period of one and one-half hours to devitrify the frit. Following devitrification, the frit was air cooled to room temperature.

30 parts of the devitrified frit were milled with 70 parts of a corrosion resistant glass frit, a mill addition, which consisted of 3 parts of clay, 0.2 parts of colloidal aluminium oxide, 0.1 part of sodium aluminate, and 43 parts water.

The corrosion resistant glass frit had the following composition in weight percent:

25	SiO ₂	73.5
	ZrO ₂	5.5
	CaO	2.0
	Li ₂ O	3.0
30	Na ₂ O	14.0
	F ₂	2.0

In the wet milling procedure, the devitrified frit and mill additions were initially melted for one hour and then the corrosion resistant frit was added and the milling was continued for an additional one and one-half hours. After milling the frit mixture had a particle size such that less than 3% was retained on a 200 mesh U.S. standard sieve.

The milled slip was then sprayed onto the ground coated surface of a low carbon steel plate and dried under infrared lamps.

The resulting crystalline-glass coated steel plate had good impact and shock resistance as well as excellent corrosion resistance.

45 WHAT WE CLAIM IS:—

1. A coated metal article comprising a base of ferrous metal or other metal having a coefficient of thermal expansion similar to that of steel, and a frit composition disposed on a surface of the base and comprising a mixture of (a) up to 60% by weight of a devitrified glass frit composed of an amorphous glass matrix containing devitrified crystalline particles, and (b) at least 40% by weight of a corrosion resistant glass frit containing 63—80% by weight of silica, said frit composition being such that when subsequently fired to fuse the composition to the metal, said amorphous

glass matrix will at least partially dissolve in said corrosion resistant glass frit during said firing.

2. A coated metal article as claimed in claim 1 wherein said devitrified glass frit comprises from 20 to 50% by weight of said frit composition.

3. A coated metal article as claimed in either of the preceding claims wherein said devitrified particles comprise 60—85% by weight of said devitrified glass frit.

4. An article as claimed in claim 3, wherein said crystalline particles have a particle size in the range of 0.1 to 2.0 microns.

5. A coated metal article comprising a base of ferrous metal or other metal having a coefficient of thermal expansion similar to that of steel, and a fused frit composition disposed on a surface of said base, the frit composition comprising a mixture of (a) up to 60% by weight of a devitrified glass frit composed of an amorphous glass matrix having dispersed therein finely divided devitrified crystalline particles which comprise at least 50% of the weight of said devitrified glass frit, and (b) at least 40% by weight of a corrosion resistant glass frit containing 63—80% by weight of silica, said amorphous glass matrix having at least partially dissolved in said corrosion resistant glass frit during firing.

6. A method of coating an article of ferrous metal on other metal having a coefficient of thermal expansion similar to that of steel, which comprises devitrifying a devitrifiable glass frit to produce a devitrified frit composed of an amorphous glass matrix and devitrified crystalline particles dispersed within said matrix, mixing up to 60% by weight of said devitrified glass frit with at least 40% by weight of a corrosion resistant glass frit containing 63—80% by weight of silica to provide a frit mixture, applying said frit mixture to the metal article and firing said article at a temperature sufficiently high to fuse said frit to said metal article, so that said amorphous glass matrix at least partially dissolves in said corrosion resistant glass frit during said firing.

7. The method claimed in claim 6, wherein said devitrifiable glass frit is devitrified by heating to a temperature of 1000° to 1600°F for 1 to 2 hours.

8. The method claimed in either of claims 6 or 7, wherein said devitrified frit comprises from 20 to 50% by weight of said frit mixture.

9. The method claimed in any of claims 6 to 8, wherein said mixing is accomplished by milling said frits together, the milled mixture having a particle size such that at least 85% by weight of said particles pass through a 200 mesh U.S. standard sieve.

10. The method claimed in any of claims 6—9, wherein said milled mixture is applied to said article in the form of a water slurry.

11. The method claimed in any of claims

6—10, including the step of drying off the water after application to said article and before firing.

12. The method claimed in any of claims
5 6 to 11, wherein said coated metal article is fired at a temperature in the range of 1400° to 1700°F.

13. The method claimed in any of claims

6 to 12, wherein said article is a steel article.

14. A method of coating an article according to claim 6 and substantially as described in Example 1 or 2 herein.

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